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Studies of the Rare-Earth Hydrides

Technical Report IV

PRESSURE-TEMPERATURE-COMPOSITION STUDIES OF THE LANTHANUM-,
CERIUM-, PRASEODYMIUM-, NEODYMIUM-, SAMARIUM-, AND
YTTERBIUM-HYDROGEN SYSTEMS. RESULTS

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Results and Discussion of Dissociation
Pressure Measurements

The entire course of an individual isotherm was ob-
tained in only a few cases. For this reason the limits of
the two-phase region are not known, except for cases like
the 800° C. isotherm for the praseodymium-hydrogen system,
and the 700° C. isotherm for the neodymium-hydrogen system.
It is apparent, however, that the dissociation pressure
plateau does not extend to the composition MH_2, but that the
isotherm tends upward below this composition, and further-
more, that this occurs at compositions lower in hydrogen at
higher temperatures. It is most likely that this region
represents a hydrogen-deficient MH_2 lattice, with some of
the tetrahedral positions not filled by hydrogen.

The first branch of the isotherms, at low composi-
tions, indicates solubility of hydrogen in the metal in
this region, which was found to extend to about $MH_{0.4}$ in a
few cases. This lower limit of the two-phase region

apparently also shifts slightly with temperature, toward higher hydrogen compositions.

In the region of the third, or steeply ascending final branch of the isotherms, hydrogen continues filling the tetrahedral holes, and the octahedral holes as well, giving a single solid phase.

It was found for each metal-hydrogen system that a plot of the logarithms of the plateau pressures versus the reciprocals of the corresponding absolute temperatures gives points falling closely upon a straight line (Figure 6). The constants A and B in the equation $\log_{10}P = A - B/T$ expressing the variation of pressure with temperature were determined for each system by the method of least squares. These equations are tabulated below, with P in millimeters and T in degrees Kelvin.

La-H: $\log_{10}P = (10.644 \pm 0.020) - (10,847 \pm 19)/T.$

Ce-H: $\log_{10}P = (10.630 \pm 0.014) - (10,761 \pm 15)/T.$

Pr-H: $\log_{10}P = (10.526 \pm 0.005) - (10,870 \pm 5)/T.$

Nd-H: $\log_{10}P = (10.482 \pm 0.028) - (11,031 \pm 28)/T.$

La-D: $\log_{10}P = (10.107 \pm 0.016) - (10,173 \pm 14)/T.$

Ce-D: $\log_{10}P = (10.205 \pm 0.006) - (10,123 \pm 6)/T.$

Pressures calculated from these equations for temperatures of 600° and 800° C. are tabulated below, as representative values:
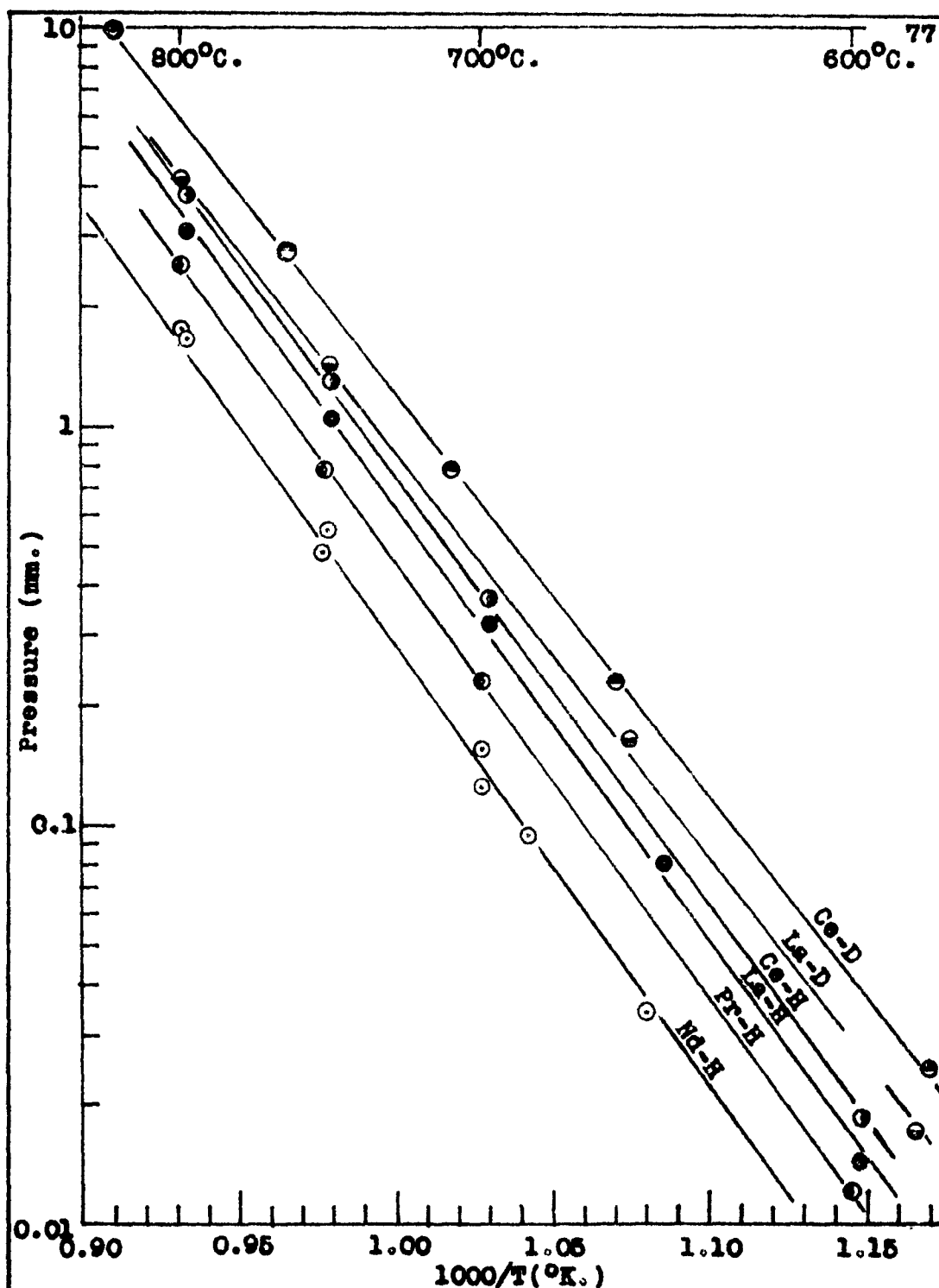
Figure 6 . Plot of logarithms of plateau pressures versus
reciprocals of corresponding absolute temperatures

System	$P_{mm}(600^{\circ}C.)$	$P_{mm}(800^{\circ}C.)$
La-H	0.0166	3.44
Ce-H	.0202	4.01
Pr-H	.0119	2.50
Nd-H	.0070	1.60
La-D	.0286	4.24
Ce-D	.0408	5.92

The limits of error given are probable errors and were found in the case of a given equation by substituting the least-squares value of one constant in the equation, together with the observed values of pressure and temperature for a particular point, and calculating the other constant. Thus the probable error r of a constant A in a particular equation may be written:

$$r = 0.6745\sqrt{\frac{\Sigma\Delta A_i^2}{n}},$$

where ΔA_i is the difference between a calculated value of A and the least-squares value, and n is the number of ex-perimentally observed points (Margenau & Murphy, 1943).

These probable errors are misleadingly small; it is of more interest to compare calculated and observed values of the pressure. This is done in Tables 1-6, where all ob-served data are listed, together with various figures used in the least-squares calculations. It is seen that the av-erage deviation of the pressure values ranges from approxi-mately 1 to 8.5%, for the various systems involved.

TABLE 1 .--Data for the log P versus 1/T plot for the
lanthanum-hydrogen system.

T^oC.	1000/T (^{o}K.)	log P	Press. Obs.	Press. Calc.	Δ P	ΔP(%)
598.	1.1478	-1.84466	0.0143	0.01563	0.00133	8.5
648.	1.0855	-1.09691	.08	.0741	.0059	8.0
698.	1.0297	-0.49485	.32	.335	.015	4.5
748.	0.9792	.02119	1.05	1.054	.004	0.4
798.	.9335	.49136	3.1	3.296	.196	5.9

TABLE 2 .--Data for the log P versus 1/T plot for the
lanthanum-deuterium system.

T^oC.	1000/T (^{o}K.)	log P	Press. Obs.	Press. Calc.	ΔP	ΔP(%)
585.	1.1652	-1.76955	0.017	0.0179	0.0009	5.0
658.	1.0741	-0.78252	0.165	.1514	.0136	9.0
750.	0.9773	.15534	1.43	1.462	.032	2.2
800.	.9318	.62325	4.2	4.246	.046	1.1

TABLE 3 .--Data for the log P versus 1/T plot for the
cerium-hydrogen system

T^oC.	1000/T (^{o}K.)	log P	Press. Obs.	Press. Calc.	Δ P	ΔP(%)
598.	1.14784	-1.73518	0.0184	0.0190	0.0006	3.2
698.	1.02965	-0.43180	.37	.355	.015	4.2
748.	0.97924	.11394	1.3	1.24	.06	4.8
798.5	.93310	.56110	3.64	3.88	.24	6.2

TABLE 4 .---Data for the log P versus 1/T plot for the
cerium-deuterium system

| T°C.	1000/T (°K.)	log P	Press. Obs.	Press. Calc.	ΔP	ΔP(%)
582.5	1.1686	-1.61439	0.0243	0.0237	0.0006	2.5
661.2	1.0702	-0.63827	.23	.235	.005	2.1
709.5	1.0176	- .10791	.78	.802	.022	2.7
762.8	0.96525	.43933	2.75	2.72	.03	1.1
825.5	.91017	.99826	9.96	9.80	.16	1.6

TABLE 5 .---Data for the log P versus 1/T plot for the
praseodymium-hydrogen system

T°C.	1000/T (°K.)	log P	Press. Obs.	Press. Calc.	ΔP	ΔP(%)
600.	1.1452	-1.92082	0.012	0.01197	0.00003	0.25
700.2	1.0273	-0.63827	.23	.2291	.0009	.39
750.	0.9773	- .10791	.78	.7998	.0198	2.54
800.	.9318	.40483	2.54	2.495	.045	1.77

TABLE 6 .---Data for the log P versus 1/T plot for the
neodymium-hydrogen system

T°C.	1000/T (°K.)	log P	Press. Obs.	Press. Calc.	ΔP	ΔP(%)
582.	1.1693	-2.39794	0.0040	0.00384	0.00016	4.2
653.	1.0797	-1.46852	.034	.0374	.0034	9.1
686.	1.0425	-1.02687	.094	.096	.002	2.1
700.	1.0275	-0.90309	.125	.141	.016	11.3
751.	0.9764	- .31247	.487	.514	.027	5.3
798.	.9335	.22272	1.67	1.53	.14	9.1
700.	1.0275	- .80967	0.155	0.141	.014	9.9
750.	0.9778	- .25964	.55	.497	.053	10.7
800.	.9318	.24551	1.76	1.60	.16	10.0
839.	.8991	.50243	3.18	3.66	.48	13.1

The reaction which occurs when hydrogen is evolved from the hydrogen-rich solid phase to give the hydrogen-poor solid phase and gaseous hydrogen may be written

$$MH_{n_\beta}(s) = MH_{n_\alpha}(s) + \frac{n_\beta - n_\alpha}{2} H_2(g)$$
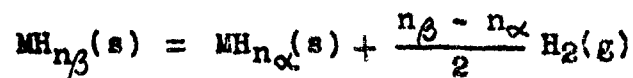
where the subscripts β and α refer to the hydrogen-rich solid phase and to the hydrogen-poor solid phase, respectively. It can be shown that the variation of the pressure with the temperature in such a system may be written in the form

$$\frac{d(\log P)}{d(1/T)} = -\frac{\Delta H}{2.3 R \left(\frac{n_\beta - n_\alpha}{2}\right)}$$

where ΔH represents the heat absorbed in the reaction written above. The perfect gas law has been assumed for hydrogen, and the change in volume of the solid has been considered to be negligible.

Since $d(\log P)/d(1/T)$ has been found experimentally to be approximately constant in the temperature range studied, the right-hand side of the equation must also be approximately constant. It is apparent from the dissociation pressure isotherms that the compositions n_α and n_β become somewhat closer together at higher temperatures. The value of ΔH must therefore also decrease at higher temperatures, since it is approximately proportional to $(n_\beta - n_\alpha)$. This

indicates also that the heat of dissociation for a given amount of hydrogen must be nearly constant. It should be pointed out that differences in the heat capacities of the reactants and products in the equation written above for the reaction introduce a variation in ΔH also.

If the equation for the reaction is re-written to indicate the evolution of one mole of hydrogen, the equation for the variation of pressure with temperature becomes

$$\frac{d(\log P)}{d(1/T)} = -\frac{\Delta H}{2.3 \, R}$$

where ΔH represents the heat of dissociation of one mole of hydrogen. If this equation is integrated, it becomes

$$\log P = -\Delta H/2.3RT + \text{constant},$$

which is equivalent to the experimentally derived relation between the pressure and the temperature. If it is borne in mind that the value of ΔH which may be determined from such an equation must vary somewhat with temperature because of the factors pointed out above, such values may nevertheless be calculated for comparison with the calorimetric data available, and with the values calculated similarly by Mulford & Holley (1955).

These heats of dissociation calculated for the various systems are tabulated below; the values of Mulford &

Holley are listed for comparison. Also listed are the calorimetric values for the heats of formation reported by Sieverts & Gotta (1928), which are not strictly comparable, since they represent room temperature values for hydrides of approximate composition $MH_{2.8}$. It may also be recalled that Dialer & Rothe (1955a, b) concluded, both from pressure-temperature-composition relationships and from calorimetric measurements of heats of solution, that the first two hydrogen atoms in cerium hydride are absorbed with the evolution of almost 50 kcal./mole H_2, and that the absorption of the third hydrogen atom evolves only 1/10 this amount.

System	Heat of dissociation (kcal./mole H_2)		Calorimetric heat of formation (kcal./mole H_2)
	This work	Mulford & Holley	Sieverts & Gotta
La-H	49.6 ± 0.1	49.7 ± 0.1	-40.09
Ce-H	49.2 ± 0.1	33.9 ± 0.8	-42.26
Pr-H	49.7 ± 0.1	47.8 ± 0.2	-39.52
Nd-H	50.5 ± 0.1	44.8 ± 0.8	
La-D	46.5 ± 0.1		
Ce-D	46.3 ± 0.1		

The limits of error given here are simply derived from the limits of error listed previously for the value of the constant B, rounded off to the nearest 0.1 kcal. (taken as a minimum in the cases of Ce-D and Pr-H in this work, where the actual deviation is less than 0.05 kcal.). They have

been listed chiefly for comparison with the data of Mulford
& Holley.

Again, it must be emphasized that such limits of
error are very misleading, and that the omission of one
point which is most off the line in a particular system
may change the values derived considerably. For example,
omission of the lowest temperature point for the La-H sys-
tem gives values of A and B derived from the other four
points of 10.232 and 10,429, respectively, and a value for
ΔH of 47.7 kcal., compared to 49.6 kcal. found above. Thus
the use of data across the entire range of temperature may
give a value of ΔH which differs by as much as 2 kcal. from
that found by omission of a point at one end. It may be
concluded that 2 kcal. would be a more sensible limit of
error on each value of ΔH listed above.

Relative dissociation pressures of hydrides and deuterides

It is a matter of some interest to compare the rela-
tive dissociation pressures of the hydrides and deuterides
for the two rare earth elements for which such data were
obtained, lanthanum and cerium.

The data available in the high pressure region show
that isotherms for the deuterides are considerably shifted
along the composition axis toward the region of lower

composition, compared to the isotherms at corresponding temperatures for the hydrides. This may be seen by comparing Figures 14 and 16, and Figures 18 and 20, in Appendix II. It is apparent that the deuterides have much higher dissociation pressures than the hydrides in this region, even though there is some uncertainty as to the actual composition values.

It is of more interest to compare the dissociation pressure values in the plateau region. Since these were not all obtained at corresponding temperatures in the different systems, it seems more to the point to refer to the plots of the logarithms of the plateau pressures versus the reciprocals of the corresponding absolute temperatures, and to compare the equations derived from these data. These equations are re-written below, with pressure in millimeters and temperature in degrees Kelvin, as before.

$$La-H: \quad \log_{10}P = 10.644 - 10,847/T$$

$$La-D: \quad \log_{10}P = 10.107 - 10,173/T$$

$$Ce-H: \quad \log_{10}P = 10.630 - 10,761/T$$

$$Ce-D: \quad \log_{10}P = 10.205 - 10,123/T$$

The dissociation pressures calculated previously from these equations at 600° C. and 800° C. are compared below.

| | Pressure | | | Pressure | |
	600° C.	800° C.		600° C.	800° C.
La-H	0.0166	3.44	Ce-H	0.0202	4.01
La-D	.0286	4.24	Ce-D	.0408	5.92
P_D/P_H	1.72	1.23	P_D/P_H	2.02	1.48

Thus a quantitative idea of the relationship of the dissociation pressure of the deuteride to that of the hydride of the same metal may be obtained. Two aspects of this relationship may be considered: 1) the higher dissociation pressure of the deuteride, and the reason for it, and 2) the manner in which the P_D/P_H ratio varies with temperature; or to put it another way, the relative values of ΔH found from the slope of the lines.

The values of ΔH for the dissociation reaction calculated from the equations listed above are re-tabulated below, in kcal./mole H_2.

La-H	49.6	Ce-H	49.2
La-D	46.5	Ce-D	46.3

The values of ΔH for the deuterides are seen to be about 3 kcal. less than for the hydrides. However, as has been discussed above, these values cannot be considered to be as accurate as indicated. Nevertheless a comparison may be made, since the data were obtained under similar conditions for the various systems.

It may first be of interest to consider what has been found in other deuteride and hydride systems. In the case of uranium, in which a dissociation pressure plateau was found to extend from 3 to 97 mole per cent UH_3, the deuteride dissociation pressure was reported to be about 1.4 times that of the hydride at all temperatures studied (Spedding, Newton, Warf, Johnson, Nottorf, Johns, & Daane, 1949). This means that the slopes of the lines in the log P versus $1/T$ plot would be the same for both the hydride and the deuteride, and the values of ΔH calculated from the simplified van't Hoff equations would also be the same. This value was computed to be 30.8 kcal./mole UH_3 (or UD_3) for the dissociation reaction. Calorimetric values at 25° C. for the formation of UH_3 and UD_3 have been reported as $-30,352 \pm 30$ and $-31,021 \pm 30$ cal./mole, respectively, by Abraham & Flotow (1955). Biegeleisen & Kant (1954) have presented a discussion to show why the ratio of the dissociation pressures of UD_3 and UH_3 in the plateau region should be independent of temperature between 530° and 700° K.

In the case of plutonium, in which a dissociation pressure plateau also exists, Mulford & Sturdy (1955) have reported that the values of ΔH calculated from the simplified van't Hoff equation are 37.4 ± 1.2 and 35.5 ± 0.7

kcal./mole for the dihydride and dideuteride, respectively,
and that the ratio P_D/P_H ranges from 1.44 at 600° C. to
1.18 at 800° C. These dissociation pressure relationships
are of the same sort as those observed for the rare earth
hydrides. Actually, the plutonium-hydrogen has been re-
ported by Mulford & Sturdy as being analogous to the
gadolinium-hydrogen system, described briefly in Chapter II.

In the alkali metal hydride systems, the deuteride
has always been found to have a higher dissociation pres-
sure than the hydride, but the data of various authors lead
to conflicting conclusions concerning the values of ΔH.

Sollers & Crenshaw (1937a, b) have reported measure-
ments of the dissociation pressures of the deuterides and
hydrides of both potassium and sodium. Heats of dissocia-
tion calculated from these data indicate that the deuter-
ides possess the higher values. These authors mentioned
that Tronstad claimed to have predicted and to have found
that the dissociation pressure of lithium deuteride was
less than that of lithium hydride, and stated their skep-
ticism of this claim. Sollers & Crenshaw further stated
that a combination of heats of dissociation as determined
from band spectra for the reactions $LiD = Li + \frac{1}{2}D_2$,
$LiH = Li + \frac{1}{2}H_2$, $D_2 = 2D$, and $H_2 = 2H$ indicated that the
heat of dissociation of LiH would be greater than that of

LiD, the reverse of that found experimentally by them for the potassium and sodium systems.

They explained the higher dissociation pressures of the deuterides as being due to the greater entropy of deuterium in the gas phase, as compared to hydrogen, and mentioned that at low temperatures differences in entropy of the solids would become relatively more important and might overbalance the effect of the difference in entropies of the gases.

Hackspill & Borocco (1939) presented data for the rubidium and cesium systems with hydrogen and deuterium, which indicated the deuterides to have smaller heats of dissociation. The various data for the systems of the alkali metals with hydrogen and deuterium are tabulated below.

	Value of ΔH (kcal./mole MH)	
System	Sollers & Crenshaw	Hackspill & Borocco
Na-H	14.4	....
Na-D	15.8	16.7
K-H	14.15	....
K-D	14.45	15.0
Rb-H	.....	10.4
Rb-D	.....	6.1
Cs-H	.....	7.9
Cs-D	.....	6.2

All these values are derived from the simplified van't Hoff

equations. Hackspill & Borocco also listed values of ΔH as found from the Nernst approximation.

Statistical mechanical calculations by Urey (1947), on the basis of spectroscopic data, indicated that for equilibria in the gas phase, the deuterides of the alkali metals Li, Na, and K would have higher dissociation pressures than the hydrides, and further that the heat of dissociation of the deuterides would be smaller than that of the hydrides. For example, values of ratios of the partition functions for NaD/NaH are 1.6908 at 273° K., and 1.1463 at 600° K., and the ratios for $(D_2)^{\frac{3}{2}}/(H_2)^{\frac{1}{2}}$ are 4.2803 at 273° K. and 1.7650 at 600° K. Thus the equilibrium constant for the reaction $NaD + \frac{1}{2}H_2 \rightleftharpoons NaH + \frac{1}{2}D_2$ is 2.5 at 273° K. and 1.5 at 600° K.

It is not readily apparent how these data can be related to the dissociation of the solid hydrides and deuterides. Various cycles may be set up, but difficulties remain, since first of all the gaseous equilibria calculations would give a free energy term, not a heat term, and further it is difficult to estimate the relative heat changes involved in the step $MH(c) = MH(g)$ for the hydride and the deuteride, even if taken through the ions as intermediates.

APPENDIX II

DISSOCIATION PRESSURE DATA

Explanatory Note

All pressures are expressed in millimeters of mercury.

The symbol "a" following a pressure reading listed in the tables indicates that the sample was absorbing hydrogen as equilibrium was being reached, and that the pressure in the system was decreasing.

The symbol "e" similarly placed indicates that the sample was evolving hydrogen as equilibrium was being reached, and that the pressure in the system was increasing.

Experimental points in the plots of pressure versus composition are represented by circles, with a short vertical line pointing either up or down, thus:

$$\delta \quad \text{or} \quad \varphi \ .$$

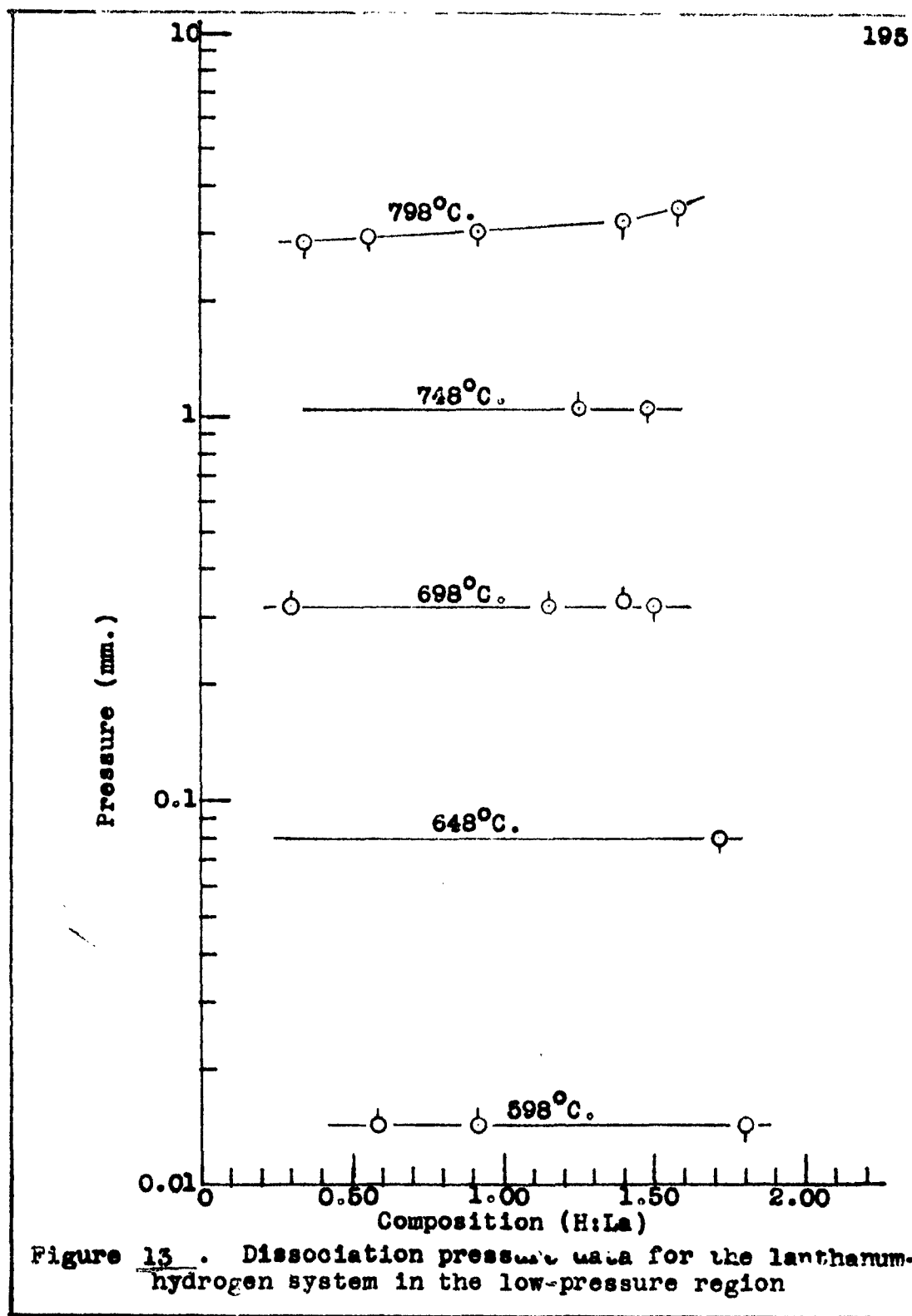The former symbol is used to represent points marked "a" in the tables, while the latter symbol is used to represent points marked "e."

TABLE 7 .--Dissociation pressure data for the lanthanum-hydrogen system in the low-pressure region

H:La	Press.		H:La	Press.	
698° C.			**598°C.**		
0.30	0.32	a	0.58	0.0143	a
1.15	.32	a	.92	.0143	a
1.40	.33	a	1.93	8.33	a
1.50	.32	e	1.80	0.0143	e
1.74	5.06	a			
798° C.			**648° C.**		
			1.72	0.08	e
1.80	27.1	e			
1.58	3.51	e	**748° C.**		
1.40	3.27	e			
0.92	3.02	e	1.48	1.06	e
.56	2.95	e	1.25	1.05	a
.34	2.86	e			

All data are from Experiment 15-61, in which the maximum absorption had reached $LaH_{2.79}$.

Figure 13 . Dissociation pressure data for the lanthanum-
hydrogen system in the low-pressure region

TABLE 8 .--Dissociation pressure data for the lanthanum-hydrogen system in the high-pressure region

H:La	Press.		H:La	Press.		H:La	Press.		H:La	Press.	
606° C.			656° C.			706° C.			756° C.		
2.27	452.	e	1.91	6.7	a	2.17	765.	e	2.11	523.	e
2.23	315.	e	1.96	18.9	a	2.16	672.	e	2.10	429.	e
2.20	223.	e	2.02	31.	a	2.13	478.	e	2.08	320.	e
2.18	159.	e	2.04	60.	a	2.12	348.	e	2.07	214.	e
2.14	87.	e	2.06	90.	a	2.11	257.	e	2.05	137.	e
2.09	49.	e	2.13	230.	a	2.07	168.	e	2.02	76.	e
2.06	29.	e	2.15	317.	a	2.05	95.	e	1.99	41.	e
2.01	12.5	e	2.17	410.	a	1.99	46.	e	1.94	18.5	e
1.99	8.5	e	2.18	491.	a	1.98	29.4	e	1.92	11.2	e
1.97	6.0	e	2.20	597.	a	1.94	18.1	e	1.90	6.9	e
2.06	31.	a	2.21	738.	a	1.91	9.4	e	1.87	4.6	e
2.15	108.	a	2.17	444.	e	1.89	6.3	e	1.85	3.3	e
2.20	196.	a	2.15	334.	e	1.85	4.2	e	1.83	2.4	e
2.23	273.	a	2.13	244.	e	1.83	2.4	e	1.81	2.1	e
			2.09	135.	e	1.81	1.8	e	1.79	1.7	e
			2.06	72.	e	1.81	2.0	a	1.92	11.1	a
			2.04	31.	e	1.98	25.5	a	1.98	31.	a
			1.98	16.	e	2.05	73.	a	2.00	67.	a
			1.94	10.0	e	2.08	185.	a	2.06	173.	a
			1.91	5.0	e	2.11	301.	a	2.07	193.	a
			1.87	3.4	e	2.14	419.	a	2.09	308.	a
			1.85	2.1	e	2.15	515.	a	2.11	417.	a
									2.12	507.	a
									2.12	544.	a

The data at 606° C. are from Experiment 7-205, in which the maximum absorption had reached $LaH_{2.92}$

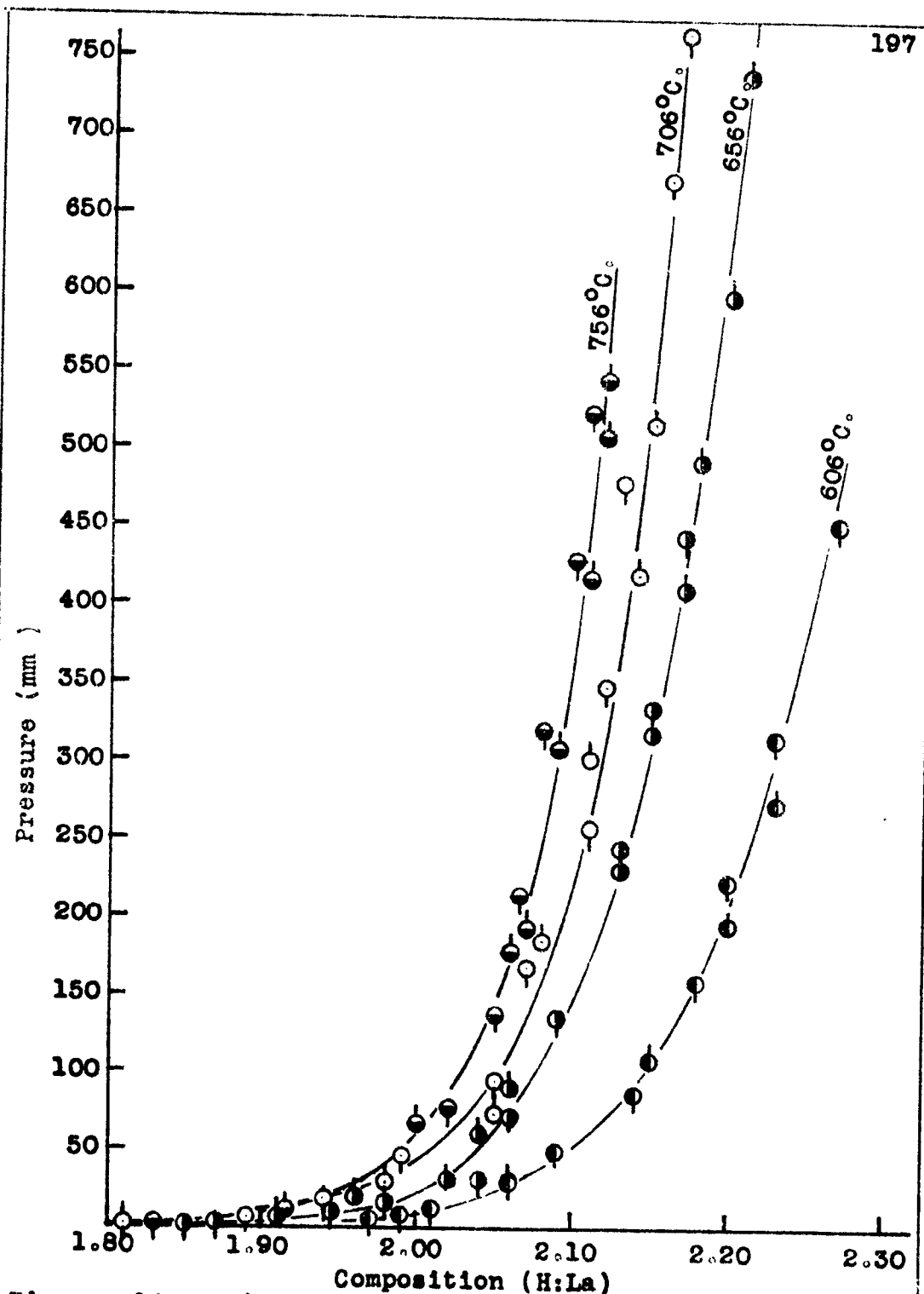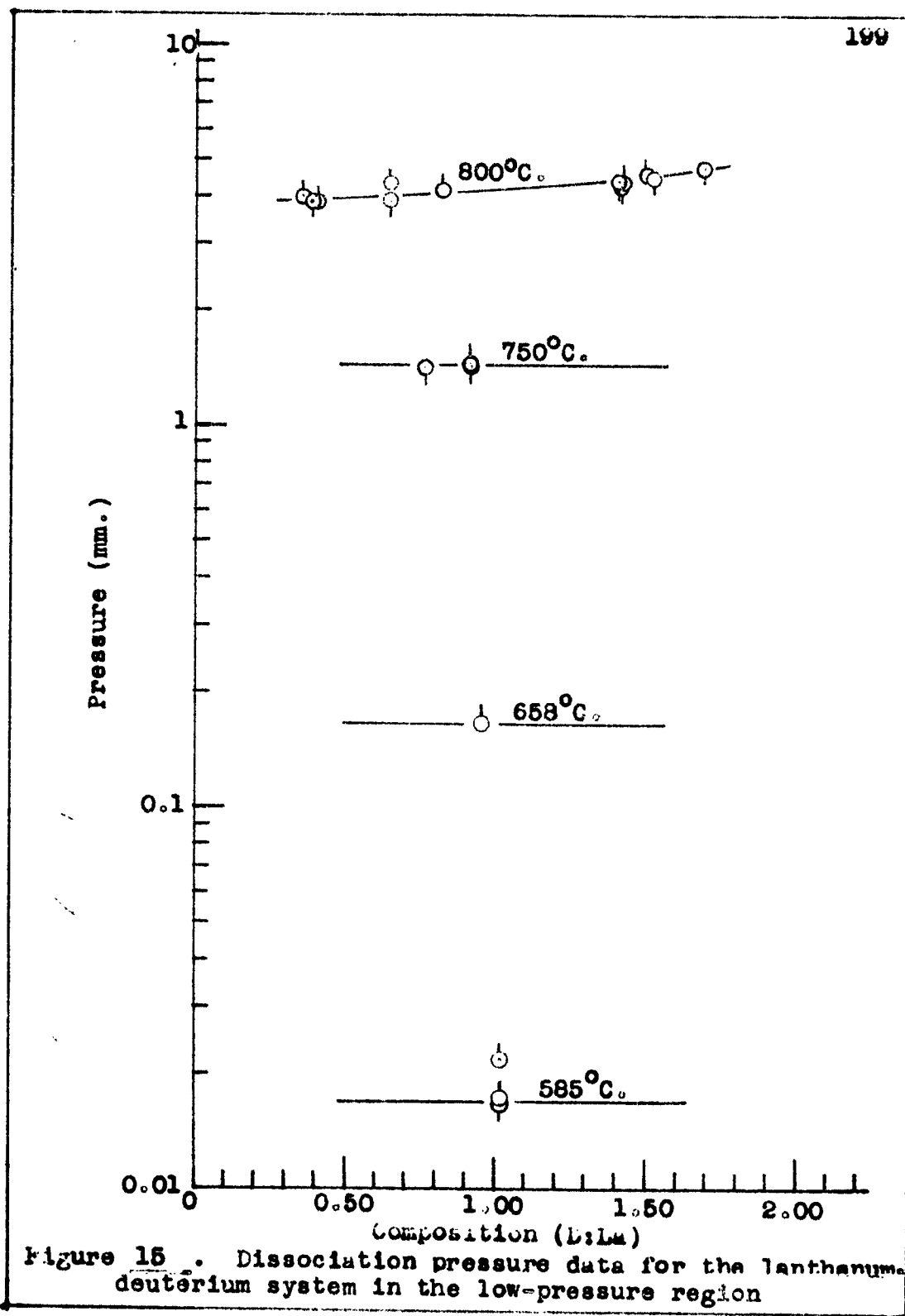All other data are from Experiment 7-210, in which the maximum absorption had reached $LaH_{2.89}$.

Figure __14__ . Dissociation pressure data for the lanthanum-
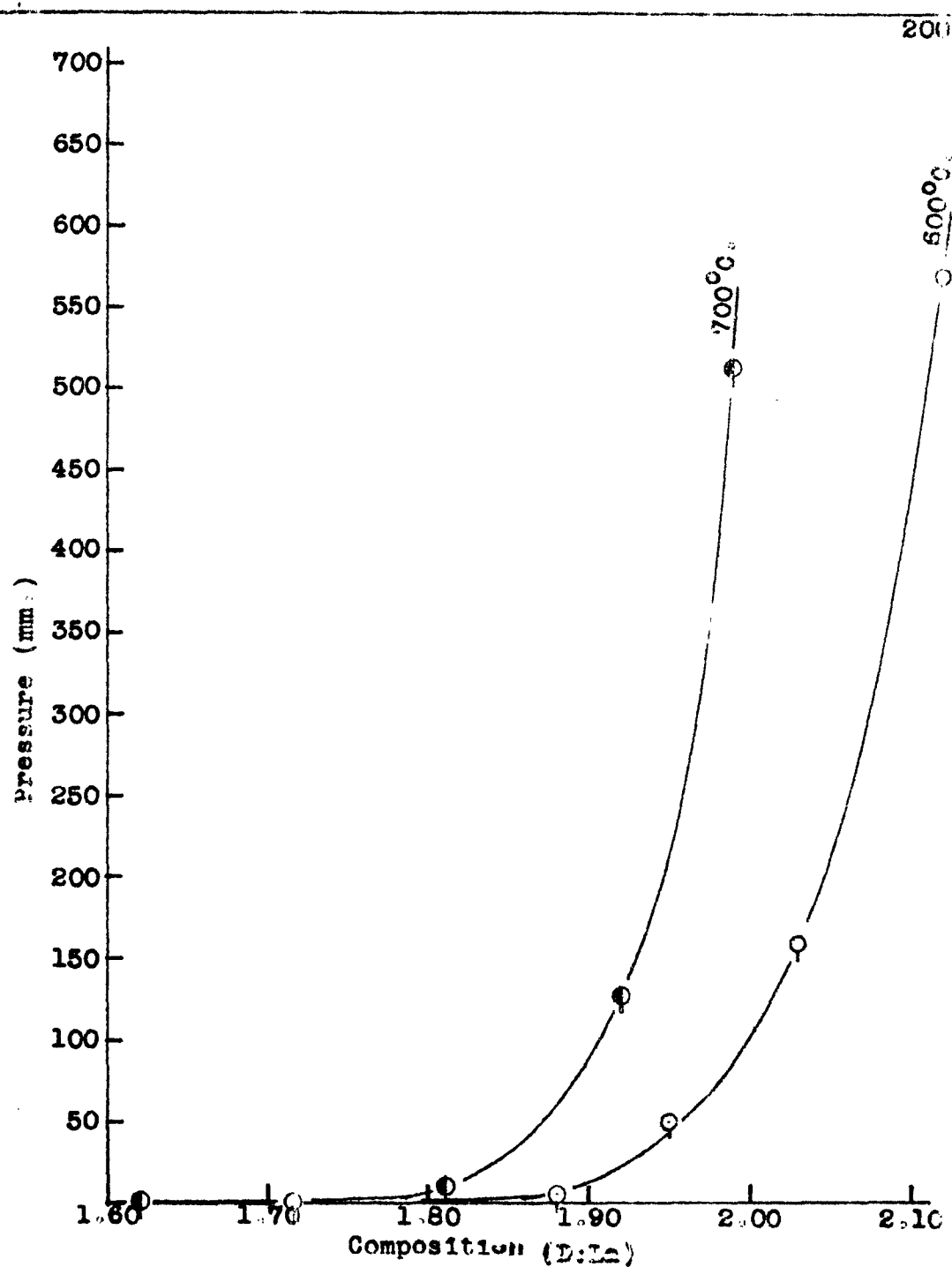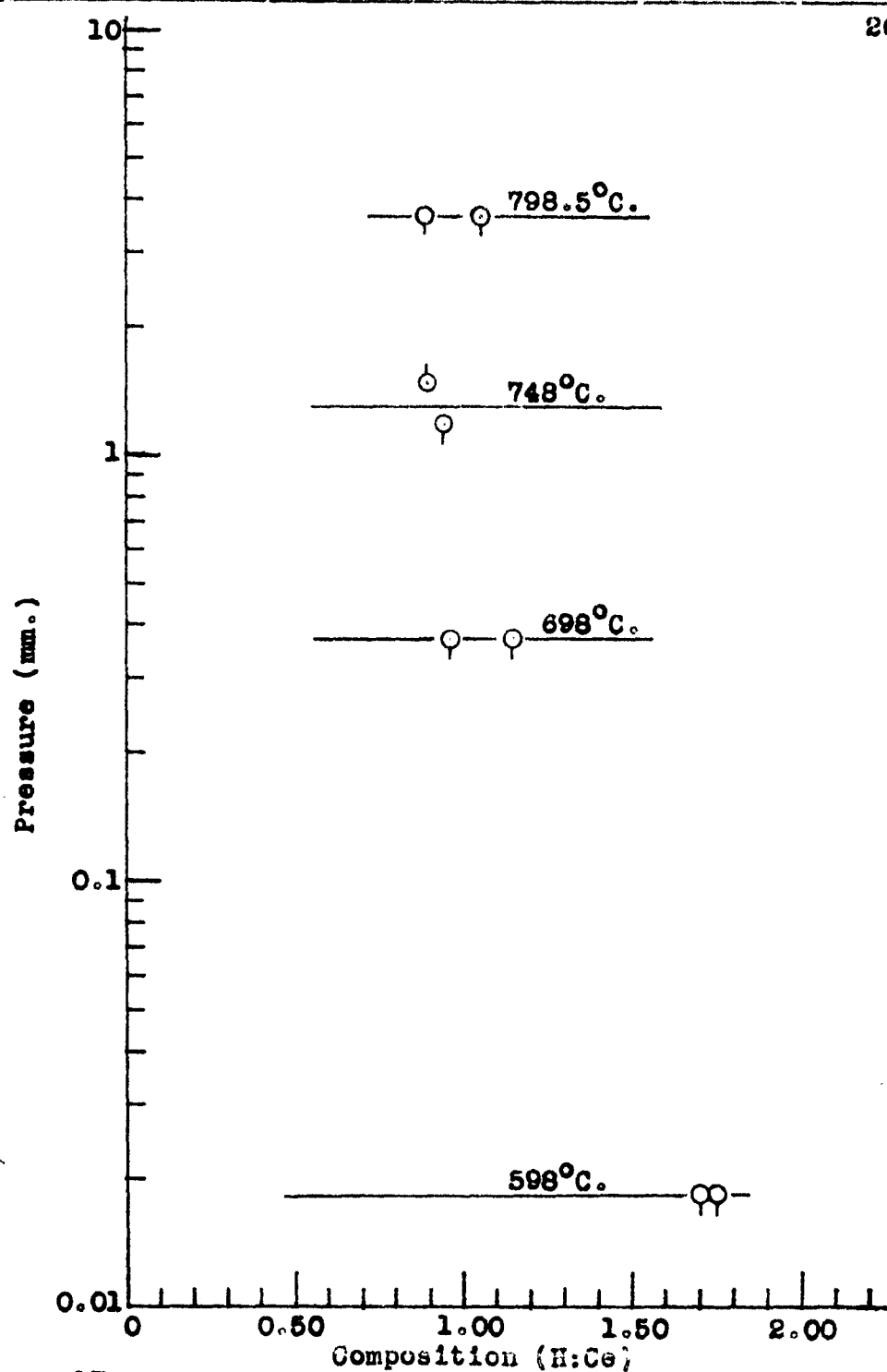hydrogen system in the high-pressure region

TABLE 9.—Dissociation pressure data for the lanthanum-
deuterium system in the low-pressure region

D:La	Press.	D:La	Press.	
800° C.		750° C.		
1.68	4.73 e	0.76	1.42	e
1.52	4.47 e	.91	1.45	a
1.40	4.35 e	.91	1.41	e
1.49	4.55 a	657.8° C.		
0.02	0.020e			
.35	3.98 a	0.95	0.165	a
.41	3.84 a	585° C.		
.38	3.87 e			
.64	4.31 a	1.02	0.0219	a
.64	3.89 e	1.02	.0173	a
.82	4.14 a	1.02	.0168	e
1.42	4.34 a			
1.41	4.23 e			

All data are from Experiment 15-99, in which the maximum absorption had reached $LaD_{2.66}$.

TABLE 10.—Dissociation pressure data for the lanthanum-
deuterium system in the high-pressure region

D:La	Press.	D:La	Press.
600° C.		700° C.	
2.12	583. e	1.99	513. e
2.03	159. e	1.92	127. e
1.95	50.2 e	1.81	10.5 e
1.88	5.2 e	1.62	1.4 e
1.73	0.6 e		

All data are from Experiment 6-195, in which the maximum absorption had reached $LaD_{2.82}$.

Figure 15 . Dissociation pressure data for the lanthanum-
deuterium system in the low-pressure region

Figure 16   Dissociation pressure data for the lanthanum–deuterium system in the high-pressure region

TABLE 11.--Dissociation pressure data for the cerium-
hydrogen system in the low-pressure region

H:Ce	Press.	H:Ce	Press.
598° C.		798.5° C.	
1.75	0.0184 e	1.05	3.63 e
1.70	.0184 e	0.88	3.64 e
698° C.		748° C.	
1.14	0.37 e	0.89	1.48 a
0.96	.37 e	.94	1.19 e

All data are from Experiment 15-55, in which the max-
imum absorption had reached $CeH_{2.74}$.

Figure 17.   Dissociation pressure data for the cerium-
hydrogen system in the low-pressure region

TABLE 12.—Dissociation pressure data for the cerium-
hydrogen system in the high-pressure region

H:Ce	Press.		H:Ce	Press.		H:Ce	Press.	
550° C.			**650° C.**			**700°C.(cont.)**		
2.38	590.	e	2.26	750.	e	2.12	122.	a
2.36	484.	e	2.25	630.	e	2.17	248.	a
2.33	328.	e	2.24	506.	e	2.20	330.	a
2.30	234.	e	2.22	382.	e	2.21	516.	a
2.25	127.	e	2.20	259.	e	2.22	644.	a
2.17	36.	e	2.15	142.	e	2.22	750.	a
2.12	13.6	e	2.11	63.	e			
2.07	5.7	e	2.07	25.3	e	**750° C.**		
2.18	43.	a	2.04	11.5	e			
2.27	173.	a	1.99	5.6	e	2.17	534.	e
2.32	330.	a	1.97	3.2	e	2.16	422.	e
2.36	494.	a	2.02	8.9	a	2.14	302.	e
2.38	643.	a	2.09	33.7	a	2.12	185.	e
2.39	761.	a	2.14	128.	a	2.09	82.	e
			2.16	181.	a	2.04	34.	e
600° C.			2.20	304.	a	2.00	14.5	e
			2.22	445.	a	1.96	5.5	e
2.34	754.	e	2.25	595.	a	1.92	3.7	e
2.31	608.	e	2.28	751.	a	2.02	18.1	a
2.28	473.	e				2.05	39.	a
2.26	342.	e	**700° C.**			2.09	115.	a
2.24	228.	e				2.13	242.	a
2.19	123.	e	2.20	510.	e	2.15	375.	a
2.13	45.	e	2.18	354.	e	2.17	498.	a
2.11	23.5	e	2.16	217.	e	2.18	632.	a
2.07	12.1	e	2.12	112.	e	2.20	762.	a
2.03	6.8	e	2.09	60.	e			
2.00	3.4	e	2.05	25.7	e			
2.14	50.	a	2.05	12.1	e			
2.22	167.	a	1.97	5.0	e			
2.25	285.	a	1.95	2.6	e			
2.28	415.	a	2.02	12.0	a			
2.31	587.	a	2.06	34.8	a			
2.32	604.	a	2.09	63.	a			

All data are from Experiment 7-237, in which the max-
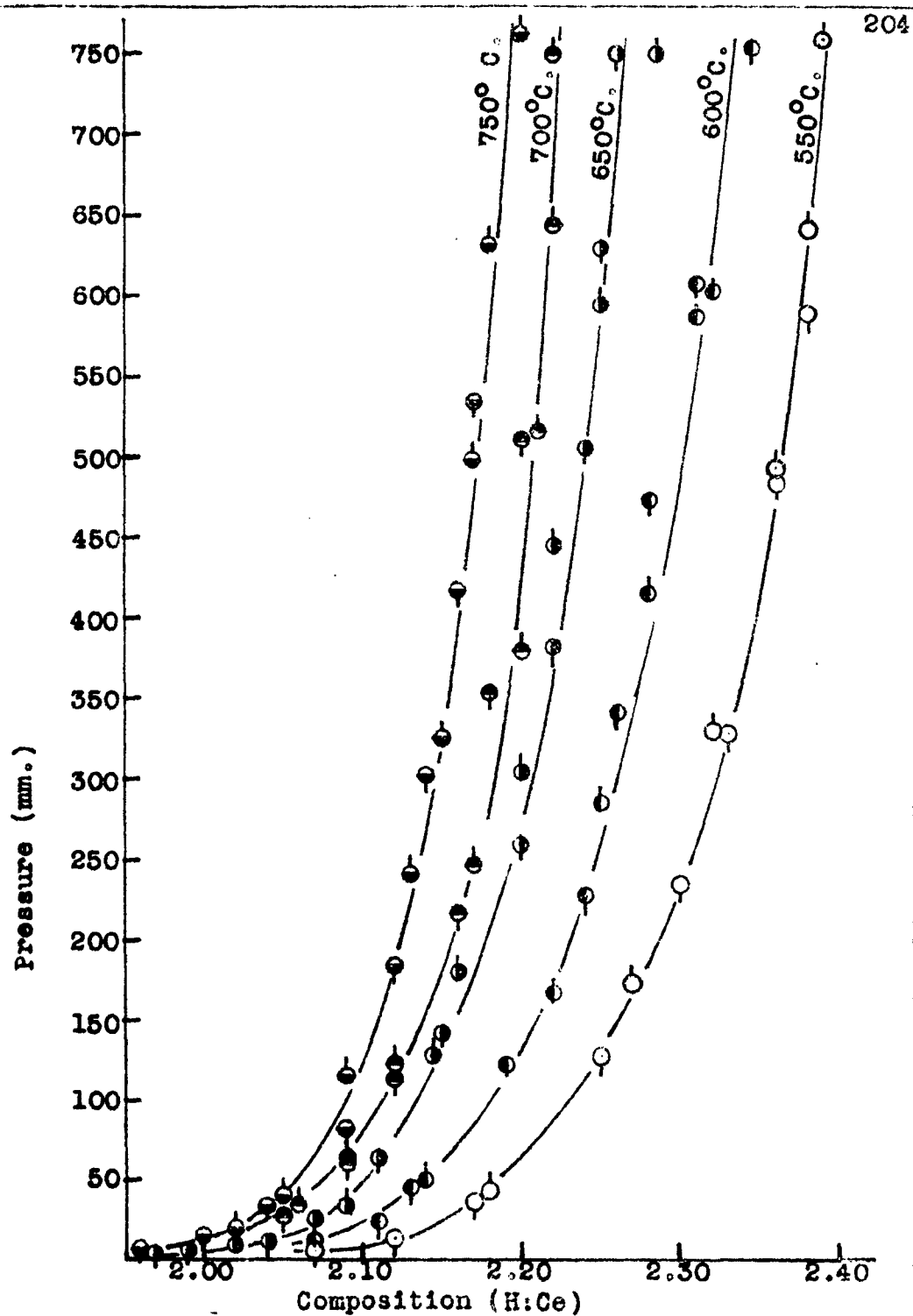imum absorption had reached $CeH_{2.92}$.

Figure 18. Dissociation pressure data for the cerium-hydrogen system in the high pressure region

TABLE 13.--Dissociation pressure data for the cerium-
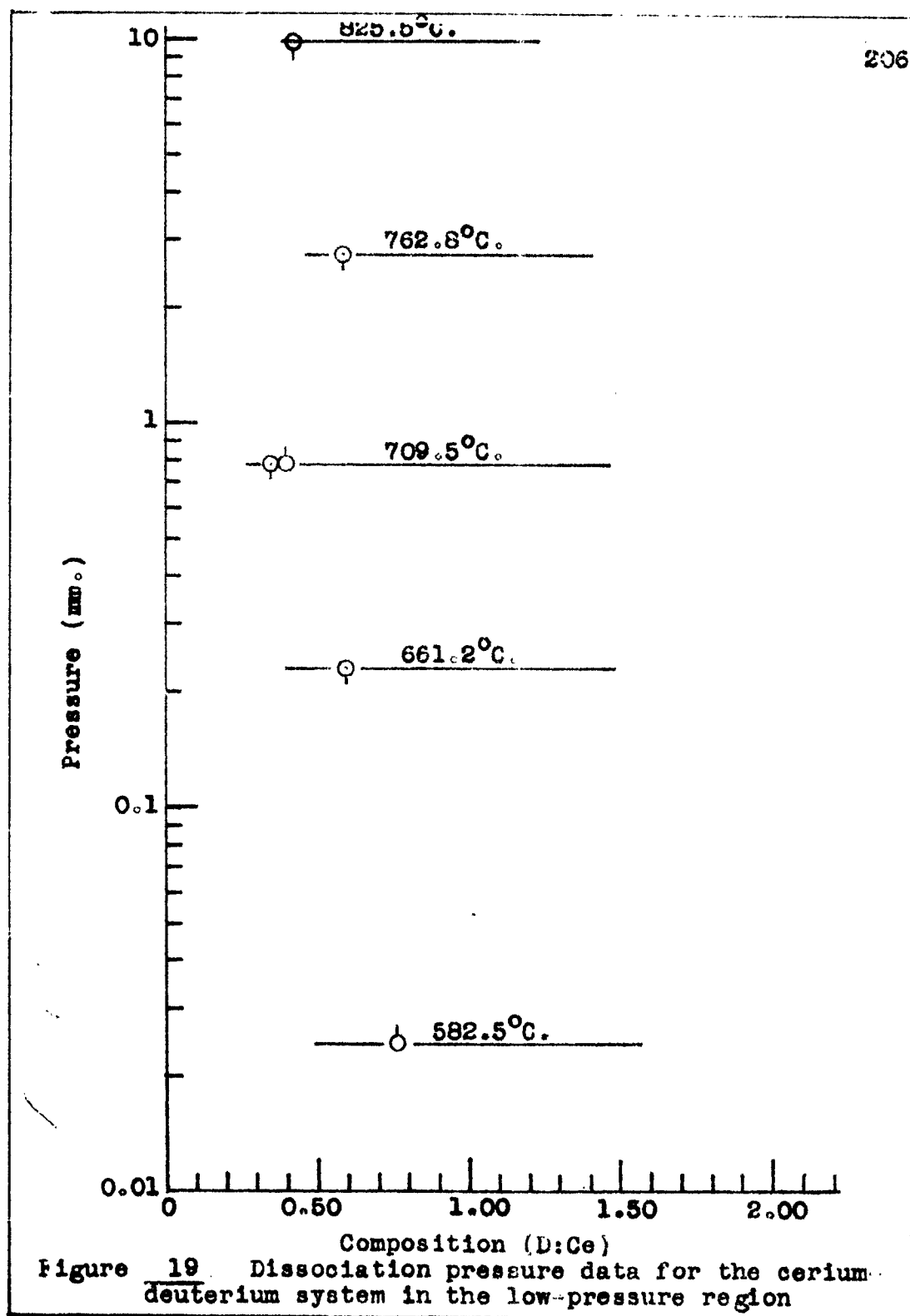deuterium system in the low-pressure region

D:Ce	Press.		D:Ce	Press.	
709.5° C.			661.2° C.		
0.34	0.78	e	0.59	0.23	e
.39	.78	a	825.5° C.		
582.5° C.			0.42	9.96	e
0.76	0.0243a		762.8° C.		
			0.58	2.75	e

All data are from Experiment 15-105, in which the max-imum absorption had reached a composition of only $CeD_{1.92}$, but at an elevated temperature. Compositions may be low by as much as 0.08. The values at 709.5° C., approached from both sides, demonstrate that these points, and therefore the others, all at higher compositions, are in the plateau region.

TABLE 14.--Dissociation pressure data for the cerium-deuterium system in the high-pressure region

D:Ce	Press.		D:Ce	Press.	
599° C.			700° C.		
2.14	552.	e	2.02	324.	e
2.07	217.	e	1.95	75.6	e
2.01	85.6	e	1.83	4.7	e
1.96	31.4	e	1.71	1.1	e
1.90	7.7	e			
1.82	1.6	e			
1.77	0.1	e			
2.12	314.	a			

All data are from Experiment 6-189, in which the max-imum absorption had reached $CeD_{2.78}$.

Figure 19   Dissociation pressure data for the cerium-
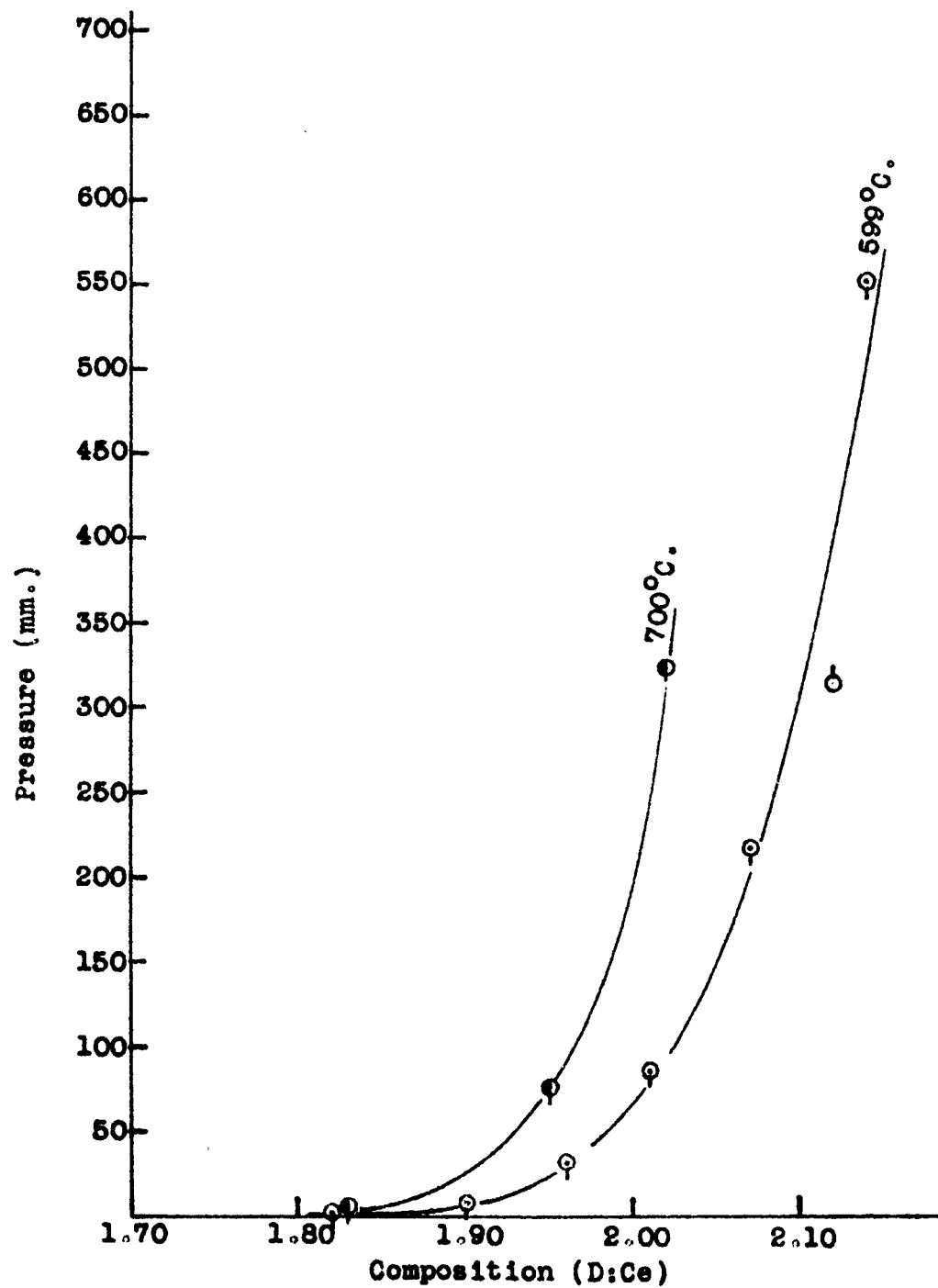deuterium system in the low-pressure region

Figure 20 . Dissociation pressure data for the cerium-
deuterium system in the high-pressure region

TABLE 15.--Dissociation pressure data for the praseodymium hydrogen system in the low-pressure region

H:Pr	Press.	H:Pr	Press.
700° C.		600° C.	
0.43	0.23 a	1.54	0.0128 a
1.24	.24 a	1.54	.0119 e
1.57	.23 e	1.78	.0138 a
		1.78	.0119 e
800° C.		1.91	.0128 a
1.70	3.26 e	750° C.	
1.58	2.51 e		
1.73	4.68 a	1.23	0.78 e
1.23	2.58 e	1.39	.78 a
1.01	2.51 e		
0.03	.14 e		
.03	.30 a		
.23	1.74 a		
.81	2.57 a		

All data are from Experiment 15-70, in which the maximum absorption had reached $PrH_{2.91}$.

TABLE 16.--Dissociation pressure data for the praseodymium hydrogen system in the high-pressure region

H:Pr	Press.	H:Pr	Press.
800° C.		600° C.	
2.02	478. e	2.08	15.9 a
1.97	279. e	2.24	123. a
1.92	101. e	2.26	319. a
1.84	14.9 e	2.29	600. a

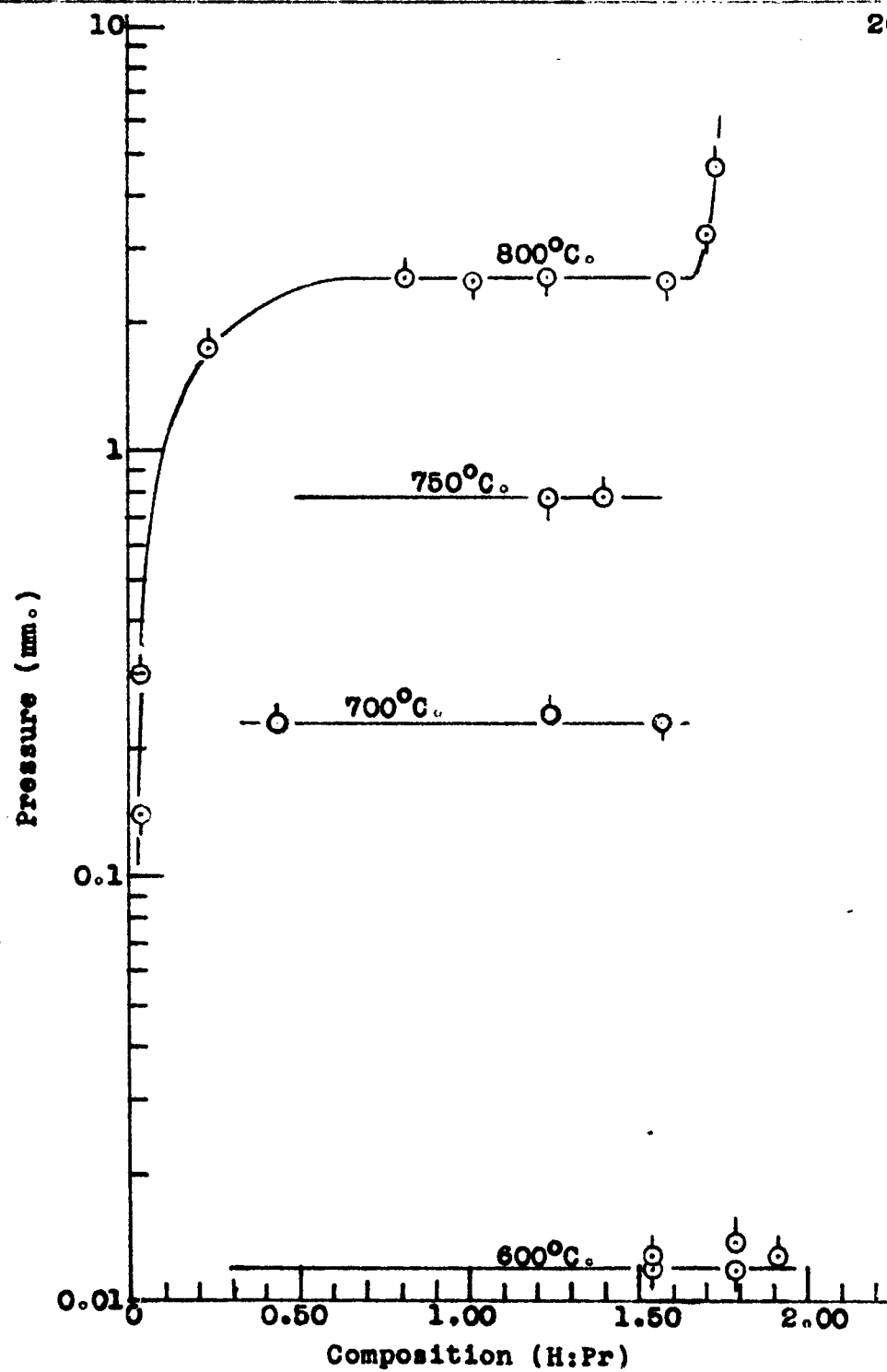All data are from Experiment 15-70, in which the maximum absorption had reached $PrH_{2.91}$

Figure __21__ Dissociation pressure data for the
praseodymium-hydrogen system in the low pressure region

Figure 22. Dissociation pressure data for the praseodymium-hydrogen system in the high-pressure region
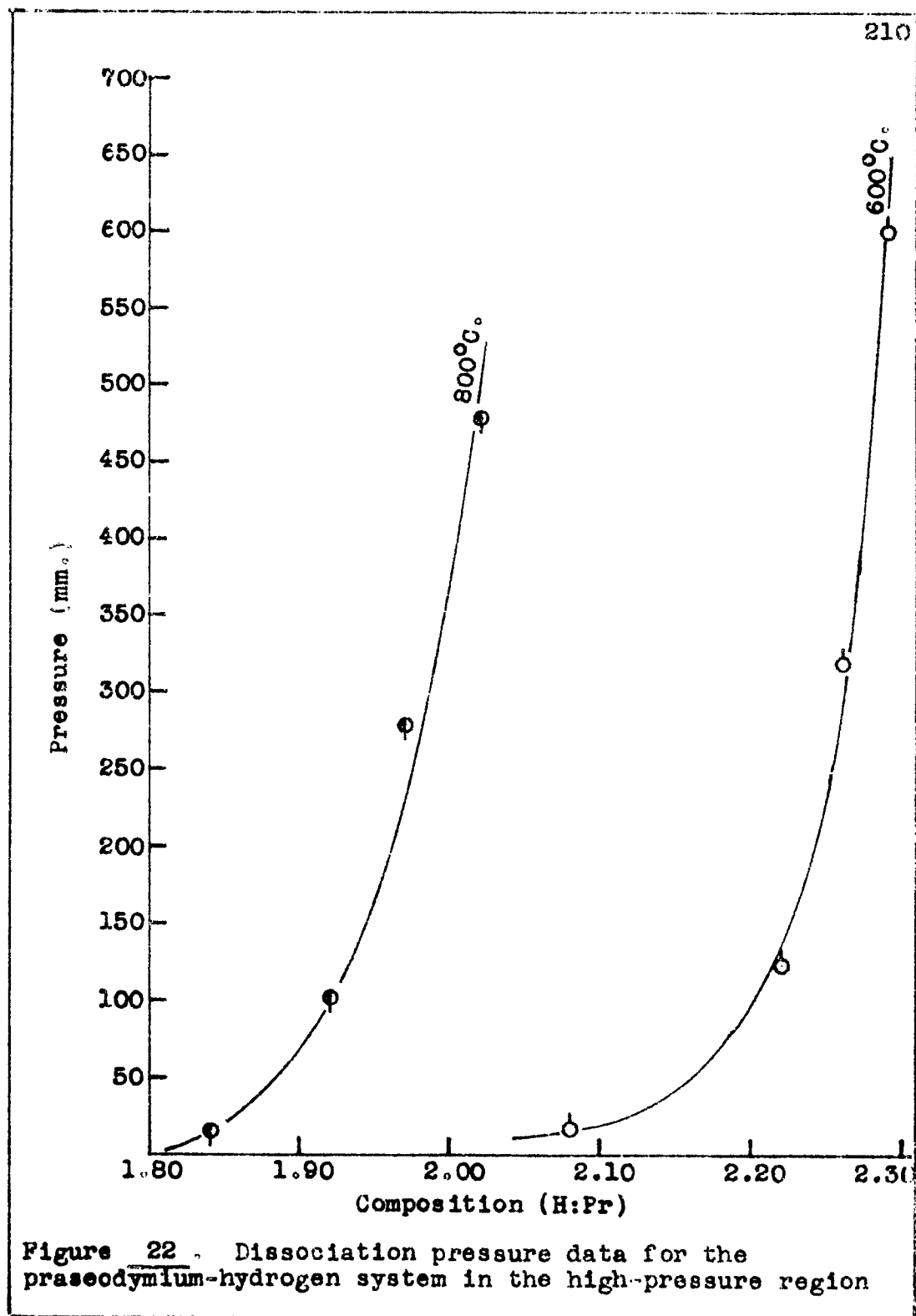
TABLE 17.—Dissociation pressure data for the neodymium-
hydrogen system in the low-pressure region

H:Nd	Press.		H:Nd	Press.		H:Nd	Press.	
700° C.			**686° C.**			**800° C.**		
1.83	0.32	e	1.30	0.094	a	1.62	3.38	a
1.82	.14	e				1.44	2.24	a
1.80	.12	e	**653° C.**			1.16	1.77	a
1.15	.120	e				0.31	1.76	e
1.10	.122	e	1.34	0.034	a	.32	1.76	a
0.92	.122	e				.23	1.76	a
.80	.122	e	**582° C.**			.23	1.76	e
.72	.118	e						
.63	.120	e	1.49	0.0040	a	**750° C.**		
.54	.119	e						
.17	.020	e	**798° C.**			0.24	0.55	a
.17	.011	e				.24	.55	e
.22	.077	a	1.28	1.67	a	.70	.56	a
.41	.123	a				.70	.53	e
.70	.124	a	**751° C.**					
.89	.124	a				**700° C.**		
1.27	.126	a	1.26	0.487	a			
1.85	.51	a				0.67	0.15	e
						.67	.15	a
						.72	.155	e
						1.03	.16	a
						1.39	.155	a
						839° C.		
						0.20	3.42	a
						.20	2.94	e

Data in the first two columns are from Experiment
7-255, in which the maximum absorption had reached $NdH_{2.89}$.
Data in the last column are from Experiment 15-89, in which
the maximum absorption had reached $NdH_{2.77}$.

Data from Experiment 7-255 are shown in the plot as
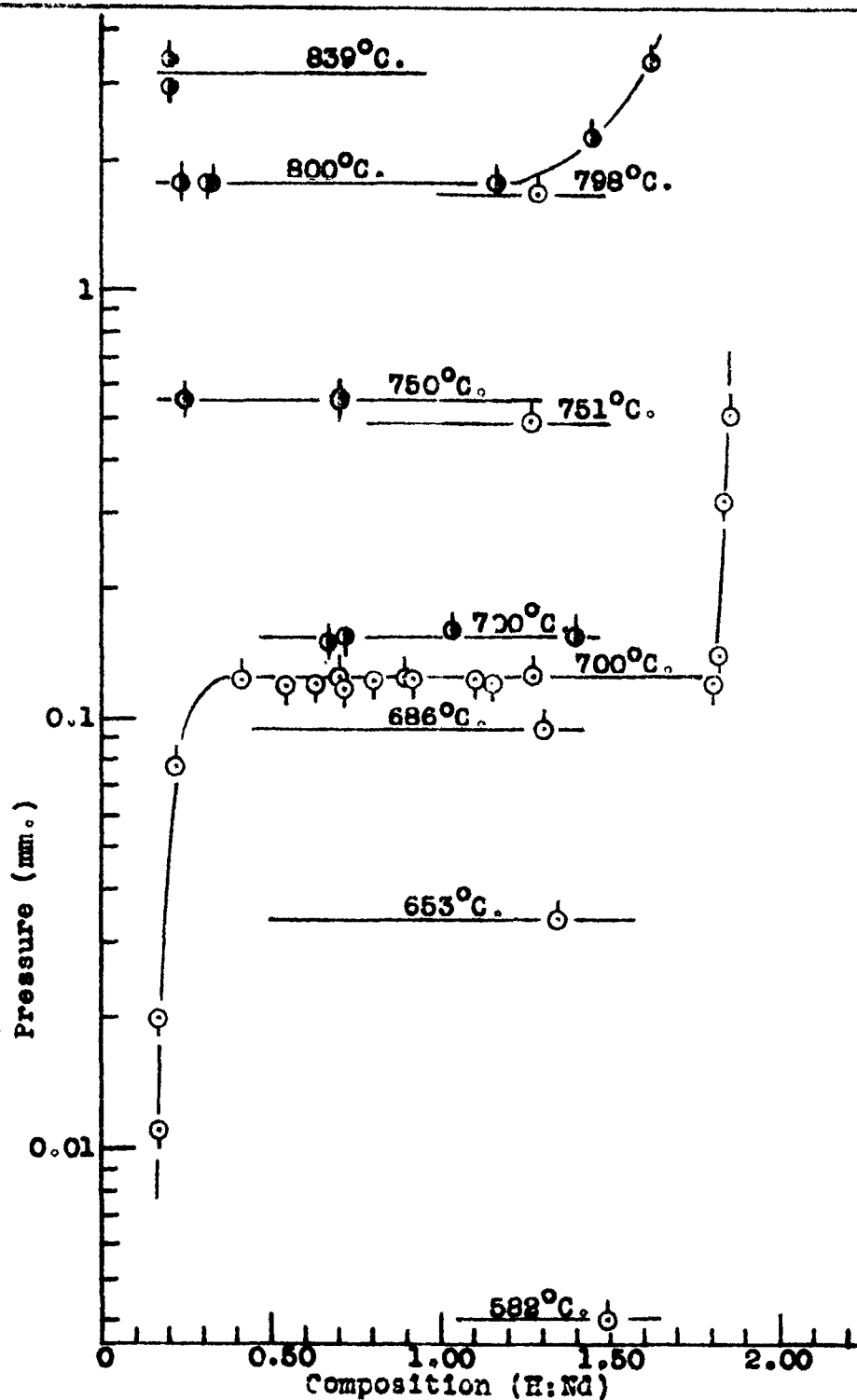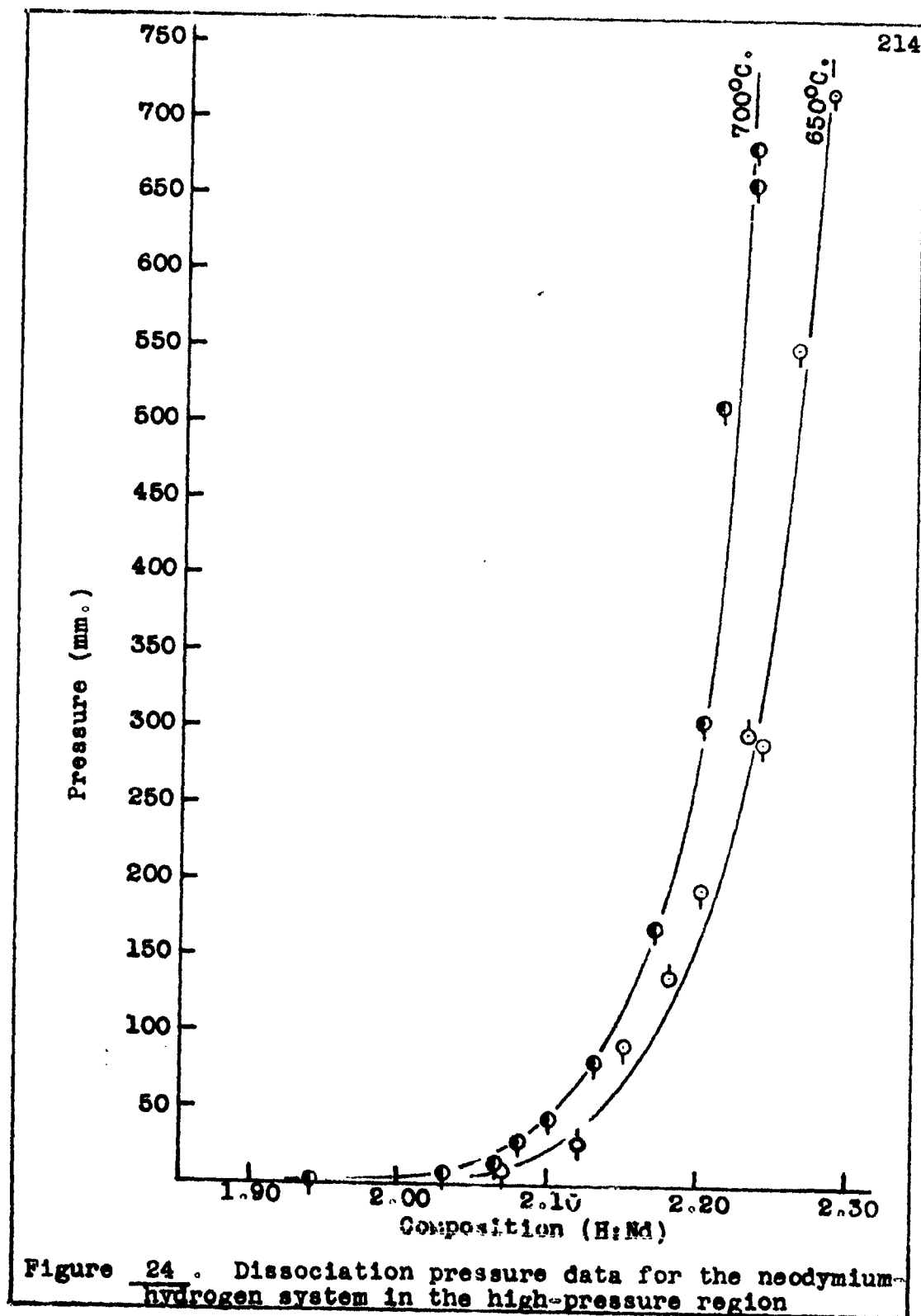open circles; data from Experiment 15-89 are shown as half-
shaded circles.

Figure 23 . Dissociation pressure data for the neodymium-
hydrogen system in the low-pressure region

TABLE 18.—Dissociation pressure data for the neodymium-
hydrogen system in the high-pressure region

H:Nd	Press.		H:Nd	Press.	
	700° C.			650° C.	
2.23	682.	e	2.28	718.	e
2.23	658.	e	2.26	550.	e
2.21	512.	e	2.24	281.	e
2.20	305.	e	2.20	194.	e
2.17	168.	e	2.15	92.	e
2.13	81.	e	2.12	28.5	e
2.10	43.	e	2.07	9.3	e
2.08	28.2	e	2.12	26.4	a
2.07	13.4	e	2.18	137.	a
2.03	6.7	e	2.23	297.	a
1.94	1.96	e			
1.92	1.42	e			

All data are from Experiment 7-255, in which the max-
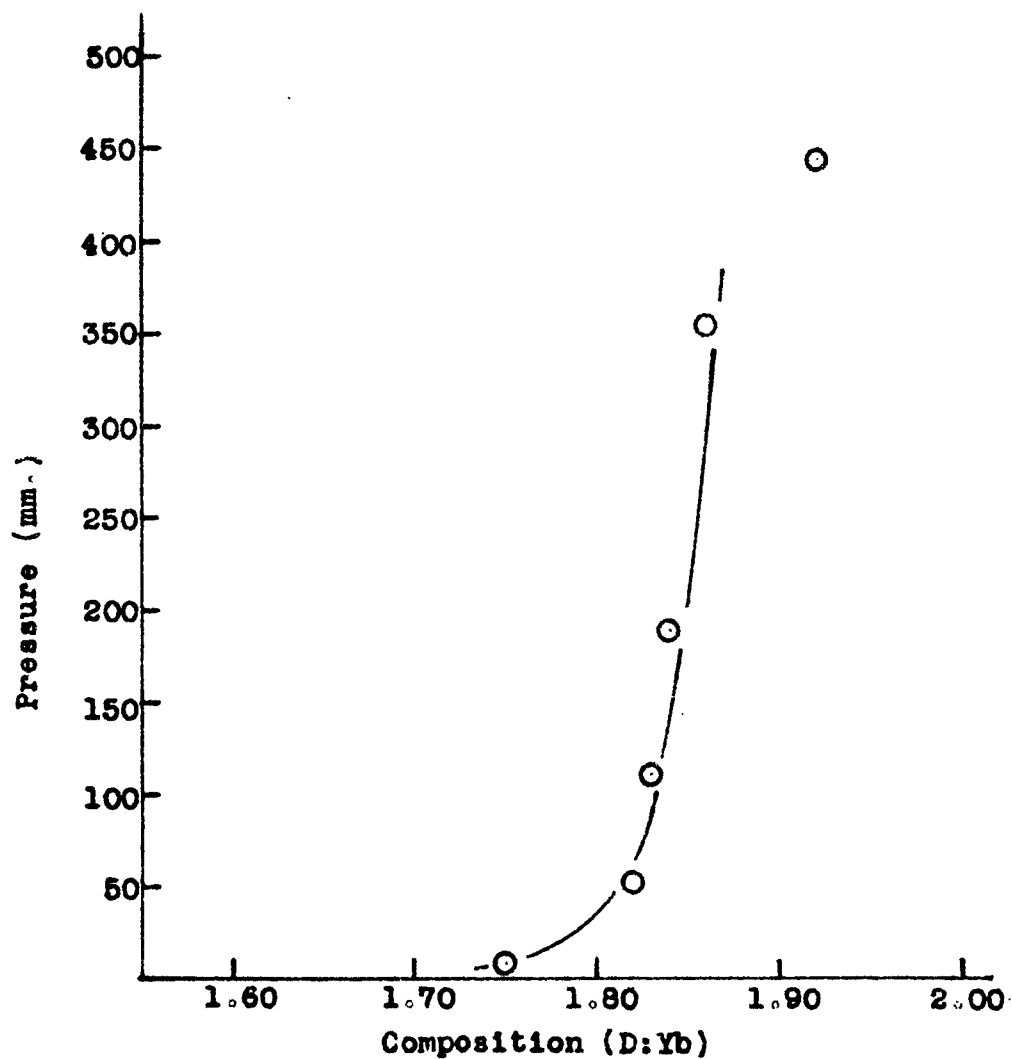imum absorption had reached $NdH_{2.89}$.

Figure 24 .   Dissociation pressure data for the neodymium-
hydrogen system in the high-pressure region

Figure **25.** Dissociation pressure data for the ytterbium-deuterium system at 600° C.

D:Yb	Pressure		D:Yb	Pressure
1.92	444 mm.		1.83	110 mm.
1.86	354		1.82	52
1.84	188		1.75	8

APPENDIX IV

THE SAMARIUM-DEUTERIUM SYSTEM

Discussion

Holley, et al. (1955) have reported that samarium hydride of composition SmH_2 has a face-centered cubic structure, with a cell constant of 5.376 ± 0.003 A. No measurements were reported for hydrides of other compositions. Mulford & Holley (1955) made no dissociation pressure measurements on the samarium-hydrogen system.

Since it was not positively confirmed in the present investigation that the behavior of samarium was completely analogous to that of the four light rare earth metals described in Chapter III, the results obtained are presented in this appendix.

A sample of samarium metal at a temperature of about 400° C. was exposed to deuterium at a pressure of about 480 mm. on the helix balance. Reaction took place over a period of about 8 minutes to a maximum composition of $SmD_{2.60}$. Some dissociation pressure data obtained at 600° C. are presented below. The high volatility of the metal prevented the obtaining of further data.
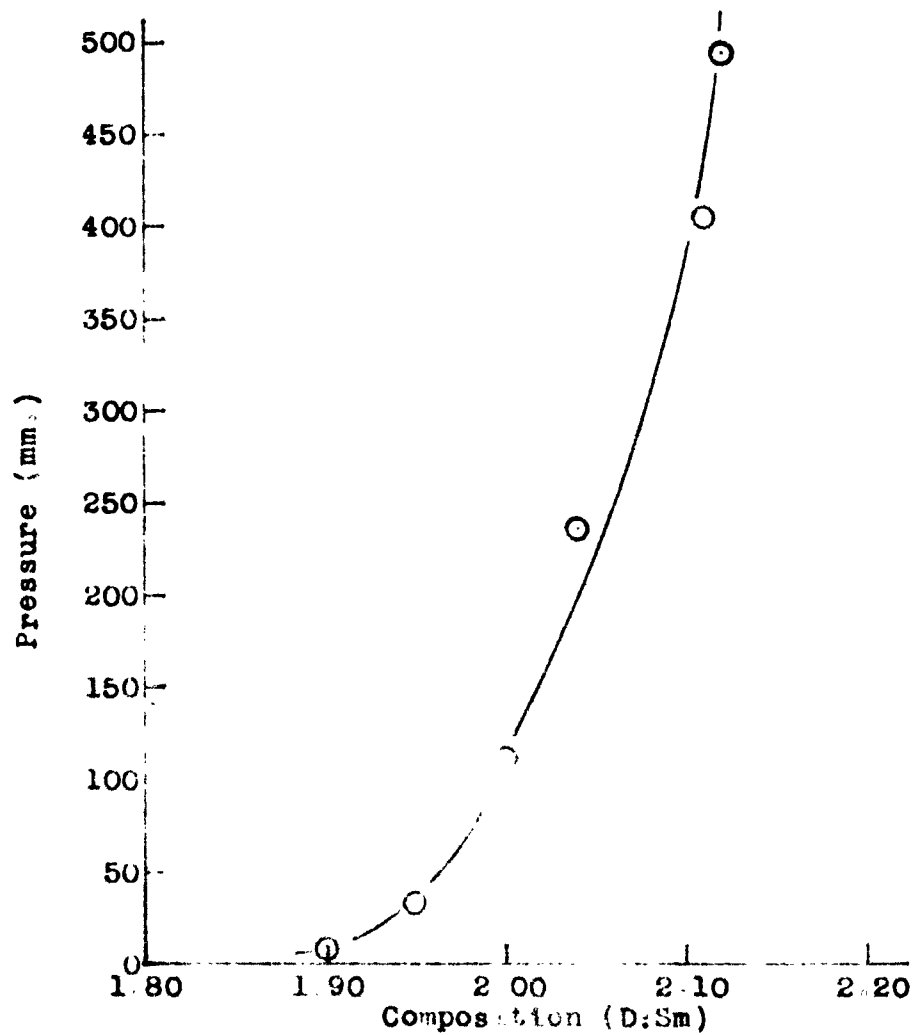
Figure 26. Dissociation pressure data for the samarium-deuterium system at 600° C.

D:Sm	Pressure	D:Sm	Pressure
2.12	494 mm	2.00	111 mm
2.11	405	1.95	33.1
2.04	236	1.90	8.0

See Technical Report I for references